

## PATENT SPECIFICATION

1.127.127



NO DRAWINGS

Inventor: HUBERT CHARLES BAILEY

Date of filing Complete Specification: 20 April, 1967.

Application Date: 26 April, 1966.

No. 18144/66.

Complete Specification Published: 11 Sept., 1968.

© Crown Copyright 1968.

OCT 8 1968

Index at acceptance:—C2 C(3A10A4C, 3A10A5C)

Int. Cl.:—C 07 c 57/04

## COMPLETE SPECIFICATION

## Stabilization of Acrylic Acid. S. PATENT OFFICE

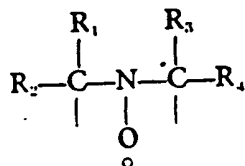
We, BP CHEMICALS (U.K.) LIMITED, formerly known as DISTILLERS CHEMICALS AND PLASTICS LIMITED, of Devonshire House, Mayfair Place, Piccadilly, London, W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the stabilization of acrylic acid.

Acrylic acid can be polymerized under controlled conditions to give useful polymers, but the monomer has a strong tendency to polymerize during preparation, recovery and storage. Various methods have been proposed for the stabilization of polymerizable monomers such as acrylic acid, e.g. the addition of p-benzo-quinone, hydroquinone or nitric oxide.

We have now found it possible to stabilize acrylic acid monomer against polymerization much more effectively than is possible by the methods mentioned above for the inhibition of the polymerization of these monomers.

Accordingly the present invention is a process for stabilizing acrylic acid against polymerization which comprises the addition of a nitroxide having the essential skeletal structure:



(I)

wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are alkyl groups and no hydrogen is bound to the remaining valencies on the carbon atoms bound to nitrogen.

The present invention is also a composition comprising acrylic acid monomer stabilized by

a nitroxide having the essential skeletal structure (I).

It has been found that the combination of acrylic acid and nitroxide of formula (I) is particularly advantageous because the nitroxide can be an effective stabilizer in the presence of oxygen and does not give undesirable coloured compounds when oxygen is present. This in marked contrast to nitric oxide, as the use of nitric oxide as a stabilizer required rigorous exclusion of oxygen from the monomer.

The addition of a controlled quantity of molecular oxygen to acrylic acid may be used to stabilize the acrylic acid against polymerization. An antioxidant may be added to the acrylic acid to give more satisfactory inhibition than is obtained by molecular oxygen alone. However if oxygen has been used to inhibit polymerization of acrylic acid and the oxygen supply is cut off, polymerization is more likely to take place than if no oxygen whatsoever had been used. This is a great disadvantage of the use of molecular oxygen as a stabilizer but it can be overcome by adding a nitroxide of formula (I) to the acrylic acid. The nitroxide is stable in the presence of oxygen but if the oxygen supply fails the presence of the nitroxide will prevent polymerization. It will be appreciated that the ability of the nitroxide to function both in the presence and absence of oxygen is a marked improvement over the prior art in which a choice had to be made between an oxygen-free and oxygen-containing system, and in which any change from one system to the other would lead to highly undesirable results.

Although as we have indicated above it is possible to stabilize acrylic acid in the presence of oxygen, for the very best results it is preferred to exclude oxygen and oxygen yielding materials from the compositions of the present invention. In the presence of oxygen peroxy compounds of acrylic acid tend to be formed, which on decomposition lead to

the consumption of nitroxide. However, the compositions of the present invention will still be stabilized against polymerisation in oxygen concentrations in the acrylic acid of up to those present in a monomer in equilibrium with air at atmospheric pressure. This is extremely useful as there is therefore no need to purge the acrylic acid with inert gas to remove dissolved oxygen. This is in marked contrast to monomers stabilized with some other inhibitors effective in the absence of oxygen. Thus nitric oxide may be used to inhibit the polymerization of monomers in absence of oxygen but where oxygen is present the inhibiting action of nitric oxide is lost.

The alkyl groups  $R_1$  to  $R_4$  may be the same or different, and preferably contain 1 to 15 carbon atoms. It is particularly preferred to use nitroxides having the essential skeletal structure (1) in which  $R_1$  to  $R_4$  are methyl, ethyl or propyl groups.

The remaining valencies of the carbon atoms in the essential skeletal structure which are not satisfied by  $R_1$  to  $R_4$  or nitrogen may be satisfied by any atom or group except hydrogen which can bond covalently to carbon although some groups may reduce the stabilizing power of the nitroxide structure (1) and are undesirable. Examples of suitable atoms

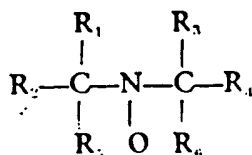
or groups are halogen, cyanide,  $-\text{C}\equiv\text{O}$  OR

when R is alkyl or aryl,  $-\text{C}\equiv\text{O}$ ,  $-\text{SPh}$ ,  $-\text{NH}_2$

$-\text{S}-\text{COCH}_3$ ,  $-\text{OCOCH}_3$ ,  $-\text{OCOC}_2\text{H}_5$ , alkenyl where the double bond is not in conjugation with the group  $-\text{N}-$  and alkyl. The



two remaining valencies which are not satisfied by  $R_1$  to  $R_4$  or nitrogen may also form part of a ring. Examples of suitable compounds having the essential skeletal structure (1) and in which the remaining valencies of (1) form part of the ring are pyrrolidine-1-oxyls and piperidine-1-oxyls. A particular example of a suitable compound in which the remaining valencies of the essential skeletal structure (1) form part of a ring is 2,2,6,6-tetramethyl-4-hydroxy-piperidine-1-oxyl. Where the remaining valencies of (1) are satisfied by alkyl groups  $R_1$ ,  $R_4$  to give a compound of formula



(II)

the groups  $R_1$  to  $R_4$  preferably contain 1 to 15 carbon atoms. Examples of suitable groups  $R_1$  and  $R_4$  are methyl ethyl and propyl groups. A specific example of a suitable compound having the essential structure (1) is di-tert-butyl nitroxide.

In a particularly advantageous embodiment of the present invention the nitroxide having the essential structure (1) is a nitroxide having between 8 and 9 carbon atoms in the molecule. Nitroxides with this number of carbon atoms in the molecule are particularly effective in suppressing "pop-corn" like polymerization which is a rapid polymerization giving rise to a very high molecular weight insoluble polymer. The formation of "pop-corn" polymer is most undesirable and materials which suppress the formation of this polymer are extremely valuable.

The monomers will not necessarily be stabilized indefinitely by the presence of the nitroxide especially when the monomer is heated as in distillation, but the acrylic acid monomer may be considered to be stabilised as long as there is a measurable increase in the time for which the monomer can be heated before polymerization starts.

Examples of concentrations of nitroxide necessary to give a satisfactory increase in stability are those between 10 and 1000 parts per million of monomer, although concentrations outside this range can be used if required.

The invention will now be illustrated by reference to the following examples:

#### EXAMPLE 1.

A solution of the polymerization initiator azo-bis (isobutyronitrile) at a concentration of  $1.2 \times 10^{-2}$  mole/litre, in freshly distilled acrylic acid containing as an additive di-tert-butyl nitroxide at the concentration shown in Table 1 was sealed under vacuum in a glass tube which was heated at 50° C.

#### EXAMPLE 2.

In a comparative example, acrylic acid compositions were prepared and heated as in Example 1 except that benzoquinone, hydroquinone and DPPH ( $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazil) at the concentrations shown in Table 1 were used in place of the nitroxide. A blank experiment in which no additive apart from the polymerization initiator was present was also carried out.

The time taken for the solutions of Examples 1 and 2 to become cloudy, due to the formation of a fine suspension of polymer particles, is also given in Table 1. Di-tert-butyl nitroxide is clearly superior in its stabilizing action to the radical scavenger DPPH and to other additives.

TABLE I

Additive	Concentration Mole/Litre	Concentration p.p.m. by wt.	Time to visible polymer formation, min.
None	0	0	1
Benzoquinone	$4.1 \times 10^{-3}$	410	1
Hydroquinone	$6.6 \times 10^{-3}$	680	1
DPPH	$1.0 \times 10^{-3}$	380	21
di-tert butyl	$2.5 \times 10^{-3}$	330	345
Nitroxide			

## EXAMPLE 3.

5 A sample of distilled acrylic acid containing the additive 2,2,6,6 - tetramethyl - 4 - hydroxypiperidine-1-oxyl at the concentration shown in Table 11 was sealed under vacuum and heated at 90° C., the time taken for particles of polymer to appear is given in Table 11.

## EXAMPLE 4.

10 In a comparative example acrylic acid solutions were prepared and heated as in Example

3, but containing the additives hydroquinone, phenothiazine and cupric chloride at the concentrations shown in Table 11 instead of the nitroxide of Example 3.

The stable nitroxide radical 2,2,6,6 - tetramethyl-4-hydroxypiperidine-1-oxyl of Example 3 is clearly superior to the known radical scavenger cupric chloride and to the other additives of Example 4.

TABLE II

Additive	Concentration Mole/litre	Concentration p.p.m. by wt	Time to Visible polymer formation, min.
None		0	2
Hydroquinone	$2.7 \times 10^{-3}$	280	1
Phenothiazine	$1.4 \times 10^{-3}$	250	69
Cupric chloride	$5.7 \times 10^{-3}$	730	435
2,2,6,6,-tetramethyl-4-hydroxypiperidine-1-oxyl	$1.4 \times 10^{-3}$	220	9,060

## EXAMPLE 5.

25 A sealed tube containing distilled acrylic acid and approximately equimolar amounts of di-tert, butyl nitroxide and oxygen at the concentrations shown in Table 111, was shaken at 90° C. The time taken for polymer particles to appear is given in Table 111.

## EXAMPLE 6.

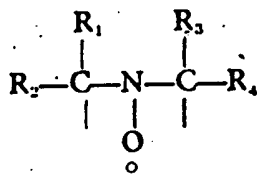
30 In a comparative example an acrylic acid solution was prepared and heated as in Example 5, but containing approximately equimolar amounts of nitric oxide and oxygen at the concentrations shown in Table 111. In the presence of oxygen di-tert butyl nitroxide is an effective stabilizer and is clearly superior to nitric oxide.

TABLE III

Di-tert butyl nitroxide concentration mole/litre	Nitric oxide concentration mole/litre	Oxygen concentration mole/litre	Time to visible polymer formation min.
$3.8 \times 10^{-4}$	0	$4 \times 10^{-4}$	195
0	$2.6 \times 10^{-3}$	$2.7 \times 10^{-3}$	2

## WHAT WE CLAIM IS:—

1. The process of stabilizing acrylic acid monomer against polymerization which comprises the addition to the acrylic acid of a nitroxide having the essential skeletal structure:



(I)

- where  $R_1$  to  $R_4$  are alkyl groups and no hydrogen is bound to the two remaining valencies on the carbon atoms bound to nitrogen.

2. The process according to Claim 1 wherein  $R_1$  to  $R_4$  each contain 1 to 15 carbon atoms.

3. The process according to claim 2 wherein  $R_1$  to  $R_4$  are methyl, ethyl or propyl groups.

4. The process according to any one of the preceding claims wherein the remaining valencies of the carbon atoms which are not satisfied by  $R_1$  to  $R_4$  or nitrogen are satisfied by alkyl radicals  $R_5$  and  $R_6$ .

5. The process according to any one of claims 1 to 3, wherein the remaining valencies of the carbon atoms which are not satisfied by  $R_1$  to  $R_4$  or nitrogen form part of a ring.

6. The process according to Claim 4 wherein the alkyl radicals  $R_5$  to  $R_6$  each contain 1 to 15 carbon atoms.

7. The process according to Claim 6

wherein  $R_1$  and  $R_4$  are methyl, ethyl, or propyl.

8. The process according to claim 7 wherein the nitroxide having the essential skeletal structure (1) is di-tert-butyl nitroxide.

9. The process according to Claim 5 wherein the nitroxide having the essential skeletal structure (1) is a pyrrolidine-1-oxyl or a piperidine-1-oxyl.

10. The process according to claim 9 wherein the nitroxide is 2,2,6,6 tetra-methyl-piperidine-1-oxyl.

11. The process according to any one of the preceding claims wherein the total number of carbon atoms in the molecule of the nitroxide having the essential skeletal structure (1) is 8 or 9.

12. The process according to any one of the preceding claims wherein the quantity of nitroxide having the essential structure (1) added to the acrylic acid monomer is between 10 and 1000 parts per million parts of acrylic acid.

13. The process according to any one of the preceding claims wherein molecular oxygen is present in amount up to that sufficient to give a saturated solution of acrylic acid at atmospheric pressure.

14. The composition comprising acrylic acid monomer stabilized by a nitroxide having the essential skeletal structure (1).

15. The process for stabilizing acrylic acid monomer substantially as herein before described with reference to the Examples.

J. HARRY,  
Agent for the Applicants,  
Great Burgh, Epsom, Surrey.